

Radiological survey in Tejo River (Portugal)

M.J. Madruga, M.M. Sequeira, L. Silva, I. Lopes,
A.R. Gomes and F. Rodrigues

*Nuclear and Technological Institute/Radiological Protection and Safety Unit, E.N. 10,
2685-953 Sacavém, Portugal
e-mail: madruga@itn.pt*

Abstract. The Tejo River flows between Spain and Portugal discharging in the Atlantic Ocean. In its Spanish section receives discharges from three nuclear power plants (NPP) being the Almaraz NPP located nearby the Portuguese border. This paper summarizes and analyses the radionuclide concentrations in surface water, sediments and fish in Tejo River from the years 2001 to 2005. The surface waters, following radiochemical procedures, were analysed for total and residual beta, ^{137}Cs and ^{90}Sr by beta measurements using proportional counters and for ^3H by liquid scintillation counting, after isotopic enrichment. Radionuclide concentrations were determined in sediments and fish by gamma spectrometry. The results obtained for ^{137}Cs and ^{90}Sr in surface waters are low and of the order of magnitude of the background. Regarding the ^3H , the activities are higher than those obtained for other rivers. The levels of artificial and natural radionuclides in fish are below the minimum detectable activity with the exception to ^{40}K . For sediments, the ^{228}Ra , ^{226}Ra and ^{137}Cs concentrations increase with the decreasing of the sediment size. An opposite behaviour was observed for ^{40}K . The data show that the radioactivity levels in Tejo River are low and within the values measured in other Portuguese rivers except for ^3H in water which values are higher due to the influence of the Almaraz NPP.

1. INTRODUCTION

The surveillance of Tejo River as so as of the main Portuguese hydrological basins is integrated in the national radiological environmental programme performed at ITN [1] in the framework of the EURATOM Treaty Article 35.

The Tejo River has its origin in Spain and flows between Spain and Portugal discharging in the Atlantic Ocean in Lisbon. In its Spanish section receives discharges from three NPP plants being the Almaraz NPP located close (about 100 km) to the border of Portugal in the region of Extremadura. At the Portuguese territory this river has been, since several years ago, regularly submitted to a radiological survey in order to evaluate the levels of radioactivity in the ecosystem [2–4] and to detect any occasional change of the NPP's normal operation.

This paper presents and discusses the results of artificial and natural radionuclide concentrations in surface water, sediments and fish in Tejo River, during the years 2001 to 2005.

2. MATERIAL AND METHODS

2.1 Sampling procedures

Surface waters (collected according to ISO 5667-5 [5]) and sediment samples (using a Berthois cone) were collected monthly at V. Velha de Ródão (sampling point in Portuguese territory close to the border) and Valada (location used as water supply of Lisbon region) and on a quarterly basis at Fratel and Belver reservoirs. The sampling was performed in the middle of the river in water flowing locations. When the river conditions did not allow this sampling procedure the samples were taken at the river bank, at the

same locations. The fish samples were collected monthly at V. Velha de Ródão by a local fisherman. The sampling locations are presented in Fig. 1.

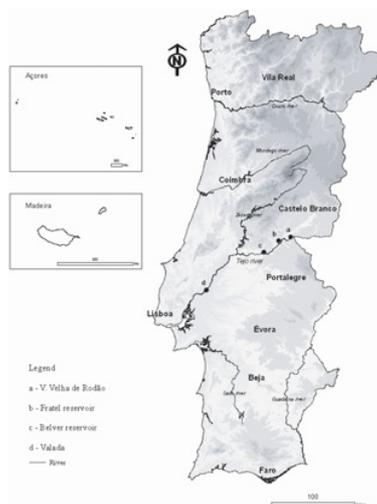


Figure 1. Sampling locations in Tejo River.

2.2 Analytical procedures

2.2.1 Waters

The surface water samples are filtered ($\phi \leq 0.45 \mu\text{m}$) and the gross beta, ^{137}Cs , ^{90}Sr and ^3H concentrations determined in the soluble phase, using radiochemical methods followed by beta measurements.

The experimental procedure of gross beta determination is according to Portuguese Standard NP 4330 [6]. Acidified water samples are evaporated to approximately 50 mL and then the radionuclides are precipitated by addition of 1 mL of concentrated sulphuric acid. The samples are calcined at 350°C , over one hour. The residue is transferred to steel planchets of 50 mm diameter and the measurement of beta activities performed with a α/β gas proportional counter (Tennelec, Canberra) calibrated with beta standards (^{40}K).

The methodology for ^3H determination is based on Portuguese Standard NP 4362 [7] with addition of isotopic enrichment. The water samples are purified by distillation, followed by isotopic enrichment procedure using electrolysis through direct current. After the neutralization procedure by the addition of PbCl_2 , a new distillation is performed in order to separate the PbO from the water. Afterwards, one aliquot of 8 mL (pH value ranging from 5 to 7) is withdrawn to a glass scintillation vial with 12 mL of Ultima Gold LLT scintillation cocktail (Packard) and then, the samples are measured in a Liquid Scintillation Counter (Beckman LS 6500). The counting efficiency is evaluated with tritiated water standards (Amersham).

Concerning to ^{90}Sr and ^{137}Cs determinations the experimental procedure consists in successive separations and purifications of the sample, being the ^{90}Sr fixed in Sr- resin (Eichrom) and the ^{137}Cs in phosphomolybdic acid ammonium salt hydrate. The sample activity is determined by beta measurements using a low-background beta system, RISO, with gas flow Geiger-Müller detectors, dully calibrated for the same geometry with ^{90}Sr and ^{137}Cs standard Amersham solutions.

2.2.2 Sediments

The sediment samples are dried at 50 °C, crushed and sieved, proceeding afterwards to the determination of the whole sediment (fraction $\Phi \leq 1000 \mu\text{m}$), sand ($250 \mu\text{m} \geq \Phi > 63 \mu\text{m}$) and silt/clay ($\Phi \leq 63 \mu\text{m}$) fractions. The ^{228}Ra (determined through ^{228}Ac daughter), ^{226}Ra (determined through ^{214}Pb and ^{214}Bi daughters), ^{137}Cs and ^{40}K concentrations were determined by gamma spectrometry, after at least one month to attain the radioactive equilibrium, using HpGe detectors calibrated with standard solutions (QCY 48 and ^{210}Pb from Amersham) prepared in the same geometry as the samples. The spectra were analysed with SAMPO 90 or Genie 2000 (Canberra) Software.

2.2.3 Fish

At the laboratory, the fish samples (usually *Barbus bocagei* Steind. and *Cyprinus carpio* L.) are measured, weighed and dissected. The muscle is dried and incinerated at 450 °C. The radionuclide activities in the ash samples are determined by gamma spectrometry as described before.

3. RESULTS AND DISCUSSION

The ^{137}Cs , ^{90}Sr and ^3H annual mean activities in Tejo River water samples, collected at V. Velha Ródão, Fratel and Belver reservoirs and Valada covering the years 2001 to 2005 are given in Table 1.

It can be observed that ^{137}Cs annual means, along the years, varies from values lower than 0.5 mBq L^{-1} (2005) to $0.14 \pm 0.4 \text{ mBq L}^{-1}$ (2003) showing, from 2004 a slight tendency of radiocaesium concentration decreasing along the Tejo River. The same tendency was verified to ^{90}Sr annual mean activities with values ranging from lower than 2.2 mBq L^{-1} (2004 and 2005) to $5.0 \pm 1.3 \text{ mBq L}^{-1}$ (2001). In general, ^{90}Sr activity levels in Tejo River surface waters are higher than those found to ^{137}Cs . However, the ^{137}Cs and ^{90}Sr concentrations are within the levels measured in previous years [2] and are in the same order of magnitude of the values obtained in other Portuguese rivers that are not influenced by any artificial radioactive sources [3].

The ^3H monthly activities in surface water samples collected at V.V. Ródão and Valada from 2001 to 2005 are presented in Fig. 2. It can be observed a variation with the time that is more pronounced at V.V. Ródão due to the proximity of the Spanish border and consequently more influenced by the Almaraz NPP tritium discharges. The temporal oscillation of the tritium levels has already been observed in previous year's [8] and depends on the water management in the Almaraz NPP cooling reservoir and of the dams existing along the river. A cyclic variation of ^3H concentrations in Tejo River with periods of about 12 months downstream the Almaraz NPP was also referred [9]. The ^3H levels mainly at V. V. Ródão are within the values reported to the Spanish section downstream the Almaraz NPP [9]. The decreasing of ^3H activities from V.V. Ródão to Valada (Table 1) could be explained by the tritium dilution along the river, mainly to Zêzere River water input, a tributary of Tejo River, located several kilometres downstream V.V. Ródão (Fig. 1). The ^3H concentrations in Zêzere River are lower and in general, below the minimum detectable activity (MDA), 0.8 Bq L^{-1} [3]. The gross beta annual mean values are similar at all sampling locations ranging from $0.10 \pm 0.05 \text{ mBq L}^{-1}$ (2001) to $0.23 \pm 0.07 \text{ mBq L}^{-1}$ (2002) and from $0.10 \pm 0.04 \text{ mBq L}^{-1}$ (2001) to $0.17 \pm 0.03 \text{ mBq L}^{-1}$ (2003) at V.V. Ródão and Valada, respectively.

The ^{228}Ra , ^{226}Ra , ^{137}Cs and ^{40}K mean activities covering the years 2001 to 2005 in the whole sediment ($\Phi \leq 1000 \mu\text{m}$), sand ($250 \mu\text{m} \geq \Phi > 63 \mu\text{m}$) and silt/clay ($\Phi \leq 63 \mu\text{m}$) fractions collected at all sampling locations are presented in Table 2.

It was verified that ^{228}Ra and ^{226}Ra (radionuclides of ^{232}Th and ^{238}U natural series respectively) activities are of the same order of magnitude although highest ^{228}Ra concentrations were obtained. For instance, at V.V. Ródão, the mean activities are 198 ± 5 and $247 \pm 15 \text{ Bq kg}^{-1}$ for ^{228}Ra and 104 ± 14 and $153 \pm 8 \text{ Bq kg}^{-1}$ for ^{226}Ra , to sand and silt/clay fractions, respectively. The $^{228}\text{Ra}/^{226}\text{Ra}$ ratio value

Table 1. Annual mean activities ($\pm\sigma$) of ^{137}Cs , ^{90}Sr and ^3H in water samples collected in Tejo River from the years 2001 to 2005. The number of samples analysed is presented in parenthesis.

Sampling Location	Year	^{137}Cs (mBq L^{-1})	^{90}Sr (mBq L^{-1})	^3H (Bq L^{-1})
V. Velha Ródão	2001	1.3 ± 0.6 (12)	4.3 ± 1.2 (12)	6.3 ± 4.3 (12)
	2002	1.0 ± 0.2 (12)	4.8 ± 0.8 (12)	11.2 ± 4.5 (12)
	2003	1.4 ± 0.4 (12)	2.7 ± 0.8 (12)	8.3 ± 3.9 (12)
	2004	<1.2 (12)	2.1 ± 0.8 (12)	9.1 ± 3.8 (12)
	2005	<0.6 (12)	<2.2 (12)	13.6 ± 3.0 (12)
Fratel reservoir	2001	1.1 ± 0.4 (12)	4.7 ± 1.2 (12)	4.9 ± 3.2 (12)
	2002	1.0 ± 0.3 (5)	4.8 ± 0.8 (5)	11.8 ± 4.0 (5)
	2003	1.3 ± 0.1 (4)	3.2 ± 0.5 (4)	8.2 ± 2.5 (4)
	2004	<0.8 (4)	4.3 ± 3.4 (4)	6.2 ± 2.0 (4)
	2005	<0.5 (4)	3.0 ± 3.4 (4)	13.5 ± 2.4 (4)
Belver reservoir	2001	-	-	-
	2002	1.1 ± 0.3 (4)	4.7 ± 0.3 (4)	8.5 ± 1.4 (4)
	2003	1.4 ± 0.2 (4)	3.0 ± 0.8 (4)	7.0 ± 2.4 (4)
	2004	<1.2 (3)	3.3 ± 1.7 (4)	6.1 ± 3.2 (4)
	2005	<1.6 (4)	2.4 ± 1.6 (4)	11.9 ± 4.1 (4)
Valada	2001	1.1 ± 0.4 (12)	5.0 ± 1.3 (12)	4.6 ± 3.3 (12)
	2002	1.1 ± 0.2 (12)	4.5 ± 0.9 (12)	6.3 ± 1.6 (12)
	2003	<1.2 (12)	2.6 ± 0.8 (12)	5.8 ± 2.3 (12)
	2004	<1.2 (10)	<2.2 (12)	5.7 ± 2.3 (12)
	2005	<0.6 (12)	3.0 ± 1.0 (12)	8.6 ± 2.0 (12)

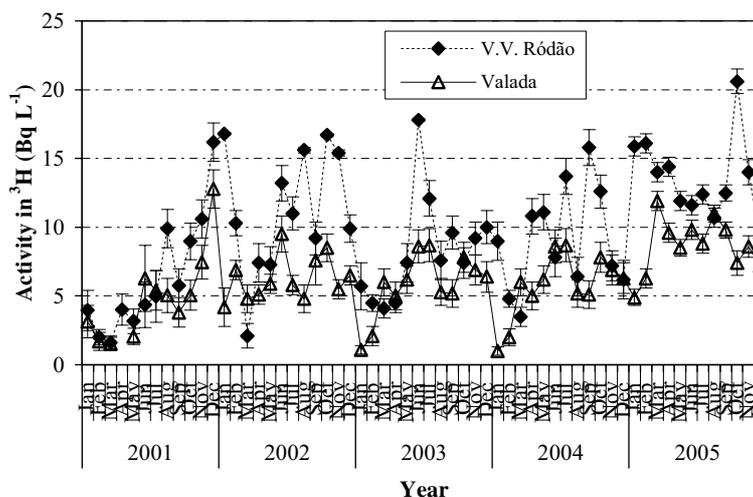


Figure 2. ^3H activities (Bq L^{-1}) in waters collected at V.V. Ródão and Valada during the years 2001 to 2005.

is higher than 1 indicating a lower degree of solubility and consequently a lower geochemical mobility of ^{232}Th when compared to ^{238}U . Similar results were reported for Tejo and Douro river sediments collected from the years 1976 to 1986 [10]. The ^{137}Cs mean activities are higher at V.V. Ródão and Fratel reservoir when compared to Valada. As illustrated in Table 2, it was observed an increase of natural and artificial radionuclide activities, from the whole sediment to the silt/clay fraction, with the exception to ^{40}K , where the activities decrease. The decreasing of ^{40}K concentrations on silt/clay fraction is related with the mineralogical composition of this fraction that might be poor in feldspar minerals. On the other hand, the increasing of ^{137}Cs concentrations in the silt/clay fraction is due to the preferentially

Table 2. Mean activities ($\pm\sigma$) (Bq kg^{-1} , dry weight) of ^{228}Ra , ^{226}Ra , ^{137}Cs and ^{40}K in sediment samples collected in Tejo River from the years 2001 to 2005. The number of samples analysed is presented in parenthesis.

Sampling location	Sediment fraction	^{228}Ra	^{226}Ra	^{137}Cs	^{40}K
V.Velha Ródão	$\varnothing \leq 1000 \mu\text{m}$	72.6 ± 5.5 (54)	46.4 ± 2.4 (54)	2.0 ± 0.2 (49)	920 ± 12 (54)
	$250 \mu\text{m} \geq \varnothing > 63 \mu\text{m}$	198 ± 5 (54)	104 ± 14 (54)	2.5 ± 0.2 (45)	773 ± 14 (54)
	$\varnothing \leq 63 \mu\text{m}$	247 ± 15 (54)	153 ± 8 (54)	6.7 ± 0.3 (46)	661 ± 15 (54)
Fratel reservoir	$\varnothing \leq 1000 \mu\text{m}$	52.1 ± 7.5 (21)	43.9 ± 3.5 (21)	4.3 ± 1.1 (18)	860 ± 26 (21)
	$250 \mu\text{m} \geq \varnothing > 63 \mu\text{m}$	61.0 ± 5.8 (21)	53.2 ± 3.7 (21)	4.5 ± 0.6 (18)	816 ± 20 (21)
	$\varnothing \leq 63 \mu\text{m}$	122 ± 18 (21)	88.6 ± 7.4 (21)	8.3 ± 1.0 (19)	782 ± 25 (21)
Belver reservoir	$\varnothing \leq 1000 \mu\text{m}$	36.1 ± 3.9 (15)	24.0 ± 2.1 (15)	0.9 ± 0.1 (15)	873 ± 22 (15)
	$250 \mu\text{m} \geq \varnothing > 63 \mu\text{m}$	102 ± 17 (15)	57.5 ± 7.2 (15)	1.9 ± 0.3 (15)	831 ± 25 (15)
	$\varnothing \leq 63 \mu\text{m}$	248 ± 64 (15)	185 ± 43 (15)	6.6 ± 1.0 (15)	781 ± 56 (15)
Valada	$\varnothing \leq 1000 \mu\text{m}$	34.3 ± 2.3 (57)	23.6 ± 1.3 (57)	0.9 ± 0.1 (40)	910 ± 10 (57)
	$250 \mu\text{m} \geq \varnothing > 63 \mu\text{m}$	67.7 ± 4.0 (57)	41.9 ± 2.2 (57)	1.1 ± 0.1 (45)	847 ± 12 (57)
	$\varnothing \leq 63 \mu\text{m}$	245 ± 22 (57)	150 ± 12 (57)	3.7 ± 0.2 (44)	798 ± 16 (57)

adsorption of caesium on specific sites “the Frayed Edge Sites (FES)” located at the clay micaceous particles [11]. The higher ^{228}Ra and ^{226}Ra concentrations in clay when compared with sand were also obtained in Dutch freshwater sediments [12].

The ^{228}Ra , ^{226}Ra , ^{137}Cs and ^{40}K annual mean activities in fish samples were determined. The levels of ^{228}Ra , ^{226}Ra and ^{137}Cs activities are in general below the MDA ($<2.6 \text{ Bq kg}^{-1}$ for ^{228}Ra and $<0.3 \text{ Bq kg}^{-1}$ for ^{226}Ra and ^{137}Cs) with the exception to ^{40}K , where the annual mean values range from $105 \pm 13 \text{ Bq kg}^{-1}$ (2002) to $120 \pm 4 \text{ Bq kg}^{-1}$ (2005) (wet weight).

4. CONCLUSIONS

The analysis of radioactivity levels in Tejo River waters for the years in study (2001–2005) shows a slight tendency of ^{137}Cs and ^{90}Sr concentrations to decrease along the river mainly from 2004. The ^{90}Sr activity levels in surface waters are higher than those found to ^{137}Cs .

Regarding the ^3H activity levels, higher values were observed at V.V. Ródão due to the proximity of the Spanish border and consequently more influenced by the Almaraz NPP tritium discharges. The decreasing of ^3H activities from V.V. Ródão to Valada could be explained by the tritium dilution along the river.

In what concerns the sediments radioactivity, it was verified that the radionuclide concentrations of the uranium and thorium series and of the artificial radionuclide, ^{137}Cs , increase with the decreasing of the sediment size. An inverse behaviour was observed for the natural radionuclide ^{40}K .

The natural and artificial radionuclide concentrations in fishes are below the MDA values except for ^{40}K .

It can be concluded that the radioactivity levels in Tejo River are low and within the values measured in other Portuguese rivers with the exception of ^3H levels in water which have been influenced by the normal operation of the Almaraz NPP.

References

- [1] Madruga M.J. *Applied Radiation and Isotopes*, <http://dx.doi.org/10.1016/j.apradiso.2008.04.008> (2008).
- [2] Carreiro M.C., Bettencourt A.O. and Sequeira M.M., *Radioprotection* **26** (1991) 649-663.
- [3] Carreiro M.C. and M.M. Sequeira, “Artificial radioactivity in Tagus River and radiological consequences to population” in: *International Symposium on Nuclear Energy and Environment, Beijing, China, 1996*. DGA/DPSR, ISBN 972-9392-92-7, depósito legal 105390/96.

- [4] Madruga M.J., Sequeira M.M., Lopes I. and Silva L., *Radioprotecção* **II**, 6 (2006) 40-50.
- [5] ISO 5667-5, Water Quality-Sampling, Part 5- Guidance on Sampling of Drinking Water Used for Food and Beverage Processing (1996).
- [6] NP 4330, Qualidade da Água, Medida da Actividade Beta Total em Águas não Salinas. Método por Fonte Concentrada (1996).
- [7] NP 4362, Determinação da Concentração da Actividade em Trítio, Método de Contagem por Cintilação Líquida (1997).
- [8] Baeza A., Brogueira A., Carreiro M.C., Garcia E., Gil J.M., Miro C., Sequeira M.M. and Teixeira M.M., *Water Research* **35**, 3 (2001) 705-714.
- [9] Baeza A., Garcia E., Miro C., Rodriguez A. and Sequeira M.M., *Fusion Science and Technology* **48**, 1 (2005) 488-491.
- [10] Carreiro M.C. and Sequeira M.M., *Radiation Protection Dosimetry* **24**, $\frac{1}{4}$ (1988) 133-137.
- [11] Wauters J., Madruga M.J., Vidal M. and Cremers A., *The Science of the Total Environment* **187** (1996) 121-130.
- [12] Van Der Graaf E., Koomans R., Limburg J. and De Vries K., *Applied Radiation and Isotopes* **65** (2007) 619-633.